

Response to reviewer comments (RC2)

The authors present a theoretical study of nanoparticle morphology and gas/droplet partitioning behavior of water using systems consisting of sodium chloride, water, and pimelic acid. The authors discover several parameters - sphericity and fractional surface coverage - that aptly describe chemical morphology as a function of composition and size regimes and variation in mass accommodation coefficients. The authors also report a threshold for the validity of continuum theories. The paper is well-written and is of interest to the Atmospheric Chemistry and Physics community, and is recommended for publication after the following general comments have been addressed.

Dear Reviewer,

Thanks for your careful reading of our manuscript entitled "**Microphysics of liquid water in sub-10 nm ultrafine aerosol particles**". We highly appreciate your time and valuable suggestions. Below you will find our replies to your comments.

Best wishes,

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As the authors note in Section 3.4, classical water models are known to have biases in errors in reproducing experimental surface tensions - though with SPC/E having one of the smallest errors (Vega and de Miguel, 2007). Additionally, a study (Lbadaoui-Darvas and Takahama, 2019) suggest that carboxylic acid-water dynamics are not well captured in equilibrium MD simulations and lead to deviations in predictions of water activity even above 0.95. On the other hand, the water activity calculations seem to suggest that the simulation results are in good agreement - with observations - is this due to canceling of errors (e.g., with molar volume) or the relatively small magnitude of the error in surface tension by these models?

Response to question 1 (Q1): Discussion about the water activity results. Thanks for raising this question. First of all, we would like to point out that the calculations of water activity (a_w) in dicarboxylic acid-water systems carried out by Lbadaoui-Darvas and Takahama¹ differ from those reported in our manuscript in several important ways: (1) we use different interatomic models to simulate carboxylic-acid-water systems; more precisely, we use the OPLS-AA model for dicarboxylic acid and the SPC/E model for water, whereas they used the OPLS-UA model for dicarboxylic acid and the TIP4P model for water; (2) our systems include a water-air interface, where dicarboxylic acid molecules preferentially accumulate relative to bulk liquid water, whereas they simulate organics in bulk liquid water; and (3) we calculated water activity using two different methods (umbrella sampling and the vapor-liquid coexistence method), whereas they calculated water activity using a third method (from the derivative of chemical potential vs. solute mole fraction, where the chemical potential was inferred from structural results). Therefore, differences between our water activity predictions are not unexpected.

More importantly, the calculations reported by Lbadaoui-Darvas and Takahama exclusively evaluate the Raoult effect in bulk aqueous solutions (i.e., the decrease in water activity associated with the organic solute). They find that this effect is underestimated by their MD simulations, with a resulting error in predicted water activity of up to about 5%. Our simulations, however, quantify the overall impact of both the Raoult and Kelvin effects in

nano-scale droplets. Unfortunately, we cannot precisely quantify the Raoult effect, for two reasons: (1) the Kelvin effect is much larger than the Raoult effect in our simulated systems (the expected Kelvin enhancement is up to ~250%; the expected Raoult inhibition is only up to ~10%), and (2) the bulk aqueous concentration of dicarboxylic acid in our systems is not well defined, because we study nanoscale droplets with significant organic accumulation at the interface, not bulk aqueous solutions.

We agree that SPC/E water model used in our study should underestimate the Kelvin effect, because it somewhat underestimates water surface tension (although less than most other water models, as noted by the reviewer). In our comparison with the Kelvin equation and Köhler theory, we account for this discrepancy by using the surface tension of SPC/E water, instead of that of real water, to obtain Kelvin/Köhler theory predictions of water activity.

Many of the conclusions summarize the effect of "organic loadings" but the simulations use a specific type of organic, namely pimelic acid. Many studies on the other hand suggest the importance of alcohols in marine aerosols (e.g., Russell et al., 2010). Is there reason that the authors can justify broadening the conclusion from a particular "organic acid" to "organics" generally? Other abundant dicarboxylic acids (e.g., oxalic acid) may also exhibit different bulk/surface partitioning behavior than demarcated by the sphericity factor. The main question is whether parts of the manuscript should be more clear in what is meant by "organic loading" in this work.

Response to question 2 (Q2): The choice of organic species and clarification of organic loading. Thank you for raising this important point. We justify our usage of pimelic acid (PML) as a representative of general aerosol organic compounds due to the following reasons: (1) organic species with 6 or 7 carbon and 3 or 4 oxygen atoms are important in organic aerosols: for example, online and offline spectrometer measurements of PM_{2.5} in Beijing by Zheng et al. (2021)² revealed that the carbon number of organic species in organic aerosols was distributed from 2 to 20, with the highest abundance observed for C6-C7 species, and that organics most commonly contained 3 or 4 oxygen atoms. This finding is also validated by measurements above temperate and boreal forests, where the molecular weight of organic species was predominantly in the range of 150-200 g mol⁻¹ (for reference, the molecular weight of PML is 160 g mol⁻¹).³ Furthermore, C3-C11 dicarboxylic acid (DA) species have been shown to be important contributors to total organic aerosol mass and can contribute ~50% of the total DA mass both in urban and rural areas.^{4,5} (2) As noted in our manuscript, the O/C ratio of PML (0.57) lies near the midpoint of the range commonly observed for aerosol organic materials (0.2 to 1.0) and near the value below which liquid-liquid phase separation is commonly observed in aerosol particles (~ 0.7 to 0.8 for organic-salt-water aerosols, ~ 0.6 for organic-water aerosols). Therefore, we believe PML has the potential to mimic the properties of key organic substances in nano-aerosol droplets. However, we agree that a variety of other organic species, including alcohols, other dicarboxylic acids, etc, are also present in aerosols, and that their behavior and impact on aerosol properties may differ from those evidenced for pimelic acid in our simulations (although some generality of our results is suggested, for example, by the consistency of our predicted water accommodation coefficients with values observed in other studies with different organic species, see Figure 6 in our manuscript). To clarify this, we plan to add the following paragraph to our conclusion section:

"Finally, we reiterate that our simulations use of a highly simplified proxy for aerosol organic matter as a single compound (PML). This compound was selected for its similarity to the compounds most abundantly observed in organic aerosols in terms of molecular weight (Thornton et al., 2020), number of C atoms (Zheng et al., 2021), O:C ratio (Song et al., 2018, Zheng et al., 2021), and functional groups (Zhao et al., 2018, Wang et al., 2022). Although the use of such an idealized proxy facilitates our effort to evaluate the sensitivity of aerosol properties to organic loading, future studies should examine whether our predictions can be generalized to other organic compounds (or mixtures of organic compounds) abundantly found in organic aerosols, such as alcohols or other dicarboxylic acids."

References:

Lbadaoui-Darvas, Mária, and Satoshi Takahama. "Water Activity from Equilibrium Molecular Dynamics Simulations and Kirkwood-Buff Theory." *The Journal of Physical Chemistry B* 123, no. 50 (December 19, 2019): 10757–68. <https://doi.org/10.1021/acs.jpcc.9b06735>.

Russell, L. M., L. N. Hawkins, A. A. Frossard, P. K. Quinn, and T. S. Bates. "Carbohydrate-like Composition of Submicron Atmospheric Particles and Their Production from Ocean Bubble Bursting." *Proceedings of the National Academy of Sciences of the United States of America* 107, no. 15 (2010): 6652–57. <https://doi.org/10.1073/pnas.0908905107>.

Vega, C., and E. de Miguel. "Surface Tension of the Most Popular Models of Water by Using the Test-Area Simulation Method." *The Journal of Chemical Physics* 126, no. 15 (2007): 154707. <https://doi.org/10.1063/1.2715577>.

References:

- (1) Lbadaoui-Darvas, M.; Takahama, S. Water Activity from Equilibrium Molecular Dynamics Simulations and Kirkwood-Buff Theory. *J. Phys. Chem. B* **2019**, 123 (50), 10757–10768. <https://doi.org/10.1021/acs.jpcc.9b06735>.
- (2) Zheng, Y.; Chen, Q.; Cheng, X.; Mohr, C.; Cai, J.; Huang, W.; Shrivastava, M.; Ye, P.; Fu, P.; Shi, X.; Ge, Y.; Liao, K.; Miao, R.; Qiu, X.; Koenig, T. K.; Chen, S. Precursors and Pathways Leading to Enhanced Secondary Organic Aerosol Formation during Severe Haze Episodes. *Environ. Sci. Technol.* **2021**, 55 (23), 15680–15693. <https://doi.org/10.1021/acs.est.1c04255>.
- (3) Thornton, J. A.; Mohr, C.; Schobesberger, S.; D'Ambro, E. L.; Lee, B. H.; Lopez-Hilfiker, F. D. Evaluating Organic Aerosol Sources and Evolution with a Combined Molecular Composition and Volatility Framework Using the Filter Inlet for Gases and Aerosols (FIGAERO). *Acc. Chem. Res.* **2020**, 53 (8), 1415–1426. <https://doi.org/10.1021/acs.accounts.0c00259>.
- (4) Zhao, W.; Kawamura, K.; Yue, S.; Wei, L.; Ren, H.; Yan, Y.; Kang, M.; Li, L.; Ren, L.; Lai, S.; Li, J.; Sun, Y.; Wang, Z.; Fu, P. Molecular Distribution and Compound-Specific Stable Carbon Isotopic Composition of Dicarboxylic Acids, Oxocarboxylic Acids and α -Dicarbonyls in PM_{2.5} from Beijing, China. *Atmospheric Chem. Phys.* **2018**, 18 (4), 2749–2767. <https://doi.org/10.5194/acp-18-2749-2018>.
- (5) Qi, W.; Wang, G.; Dai, W.; Liu, S.; Zhang, T.; Wu, C.; Li, J.; Shen, M.; Guo, X.; Meng, J.; Li, J. Molecular Characteristics and Stable Carbon Isotope Compositions of Dicarboxylic Acids and Related Compounds in Wintertime Aerosols of Northwest China. *Sci. Rep.* **2022**, 12 (1), 11266. <https://doi.org/10.1038/s41598-022-15222-6>.